Development of a Black Carbon Standard for Thermal-Optical Analysis

Thomas Kirchstetter, Lawrence Berkeley National Laboratory

Motivation: Carbonaceous aerosols affect air quality and climate, but measurements of black (BC) and organic (OC) carbon concentrations are very uncertain. Many variants of the thermal-optical analysis (TOA) method exist, and more than a decade of research has not resolved the differences in their estimates of OC and BC (i.e., the OC/BC split). This is largely due to the lack of a BC standard. Without a BC standard, the accuracy of TOA measurements of OC and BC cannot be determined.

Research Goal: Develop a method of producing BC standards that can be used to determine the accuracy in TOA measurements of OC and BC.

Approach: The uncertainty in TOA measurements is due to the presence of both OC and BC in particulate matter. Whereas measuring total carbon (TC) is straightforward, OC pyrolysis and charring and premature evolution of BC render determination of the OC/BC split uncertain (and method dependent) (*1,2,3*). If a particulate matter sample containing only OC or BC was analyzed by TOA, there would be little uncertainty in the measurement. Our approach to developing a standard for TOA, therefore, is to 1) generate particulate matter composed only of BC and fully characterize the physical and optical properties of the BC, 2) demonstrate that this BC can be collected in known amounts on filters and 3) reproduce filter samples with known amounts of BC mixed with other aerosol species, most notably OC. These filters, having known amounts of BC, could be used as standards for determining the accuracy of TOA measurements of BC and the OC/BC split. TOA methods could then be optimized for accuracy.

Particle Generation with an Inverted Flame

We have initiated research to generate controlled amounts of BC. The particle source is an inverted diffusion flame recently developed at Lawrence Berkeley National Laboratory. The inverted flame produces particles containing only BC, and the production rate is very stable over a wide range of BC concentrations.

The particles are composed of BC only

The particles generated by this diffusion flame contain a negligible amount of OC, as determined by (in-situ) laser fluorescence spectroscopy, which showed no evidence of unsaturated or aromatic hydrocarbons (*4*), and by TOA itself. Filter samples of the flame particles have been analyzed according to the NIOSH and IMPROVE protocols in addition to the protocol developed at Lawrence Berkeley National Lab. TOA illustrates that a) all of the carbon evolves as a single peak at high temperatures, b) the light attenuated by the particles diminishes simultaneously with the thermal evolution of the carbon, and c) charring does not occur, nor does any carbon evolve, during heating of the sample in an inert atmosphere (i.e., in helium). Thermograms from the Berkeley Lab

method are shown in Figure 1. A single, high temperature peak in the carbon thermogram indicates that all of the carbon in the sample is refractory. The overlap of the carbon and optical thermograms indicates that the carbon is entirely light absorbing BC. In this case, quantifying the amount of BC is as straightforward as measuring TC because there is no interfering OC. Last, the carbon spectra of this BC (as measured by near-edge x-ray absorption fine structure (NEXFAS) analysis at the Berkeley Lab Advance Light Source) is consistent with other combustion soot particles.

The particle generation rate is nearly constant over a wide concentration range

The inverted flame is remarkably stable. Figure 2 illustrates the stability of the number size distribution of BC particles, and Figure 3 demonstrates that that the number concentration of particles and their optical properties can be maintained at a nearly constant level for long periods of time. A wide range of BC concentrations – from micrograms to milligrams per cubic meter – are possible. Figure 4 illustrates the correlation between light scattering and BC particle number concentration over a range of concentrations.

Case Studies

We have conducted experiments that demonstrate the utility of this black carbon source.

Evaluation of TOA: Effect of Aerosol Composition on BC Analysis

We have observed that the evolution of BC during TOA can be significantly affected by other aerosol constituents. In this case, we generated external mixtures of BC and sodium chloride (NaCl). The salt particles were introduced downstream of the flame so that the production rate of BC was unaltered. This enabled the production of salt/BC mixtures in varying proportions while holding the mass concentration of BC constant, as illustrated in Figure 5. In principle, BC can be mixed with other constituents (including organics, sulfate, and nitrate) to produce filter samples of mixed aerosol composition with known amounts of BC. Figure 6 shows that the presence of NaCl in the sample decreased by 150°C the evolution temperature of BC.

This demonstrates that the evolution temperature of BC can be significantly influenced by other aerosol constituents, and thus the OC/BC split should not be determined based solely on evolution temperature. In addition, since thermogram features are influenced by the aerosol composition, the various temperature-defined EC fractions of the IMPROVE and NIOSH protocols (i.e., EC1, EC2, EC3) may not be suitable as source profiles (i.e., fingerprints) for use in source apportionment calculations.

Other Application(s): Evaluation of the Aethalometer

In addition to the development of a BC standard for TOA, our method of BC generation can be used to 1) evaluate the accuracy of (and develop a modified calibration if needed) the aethalometer and other instruments, including the single particle soot photometer, and the photoacoustic and cavity ring-down methods, and 2) quantify the effect of aerosol mixing state on climate relevant properties, namely the aerosol absorption coefficient and single scattering albedo.

Since recent studies indicate shortcomings in the calibration of the aethalometer, we conducted tests to determine the aethalometer's real time-response when exposed to a constant concentration of BC. We observed that the aethalometer reported decreasing BC concentrations (in each of its measurement cycles) despite the fact that the BC concentration was constant. The reason for the erroneous behavior is that the aethalometer calibration does not account for the fact that the amount of light attenuated by a particle-laden filter increases in less than constant proportion to the mass loading of BC on the filter. In other words, the aethalometer treats the attenuation coefficient as a constant when it actually varies with filter loading. We developed a modified calibration of the aethalometer, based on the BC concentration measured by TOA, to correct the aethalometer data, as shown in Figure 7.

References:

1. Currie, LA; et al. A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a, *J. of Res. NIST*, *107*, 279-298, 2002.
2. Schmid, H; Laskus, L; Abraham, HJ; et al. Results of the "carbon conference" international aerosol carbon round robin test stage I, *Atmos. Environ., 35*, 2111-2121, 2001.
3. Shah, JJ; Rau, JA, Carbonaceous species methods comparison study: Interlaboratory round robin interpretation of results. Final report to Research Division, California Air Resources Board, Sacramento, California, 1991.
4. Stipe, CB; Higgins, BS; Lucas, D; Koshland, CP; Sawyer, RF, Inverted co-flow diffusion flame for producing soot, *Rev. Sci., Instruments*, 76, 023908, 2005.

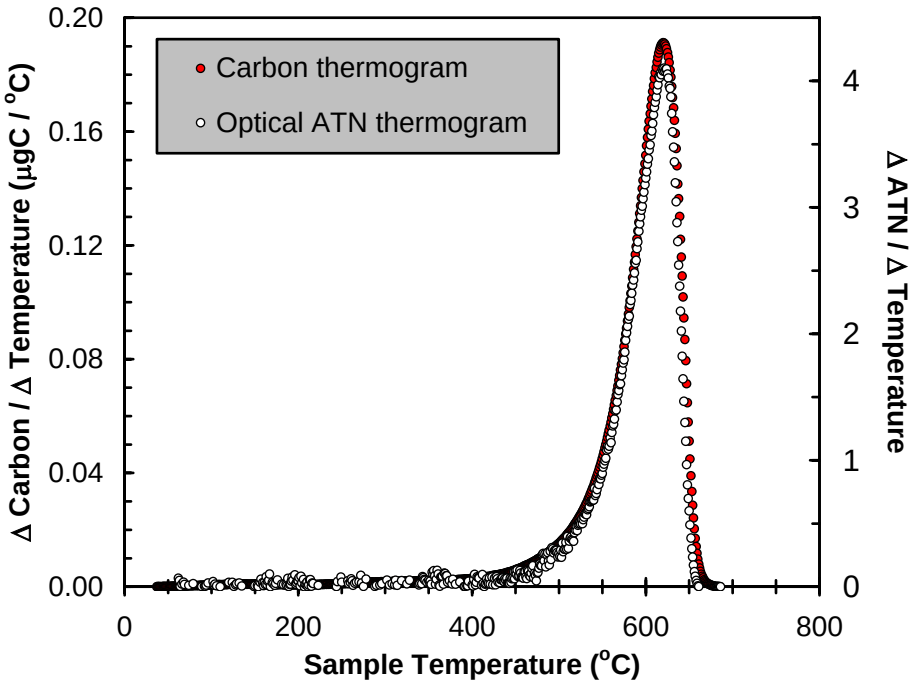

Figure 1. Thermal-optical analysis (in oxygen) of a diffusion flame particles. A single carbon peak at high temperature evolves simultaneously with the change in particle light absorbance. The overlap of the carbon and optical thermograms indicates that the carbon is entirely light absorbing. The flat portion of the thermograms indicates the absence of OC and charring.

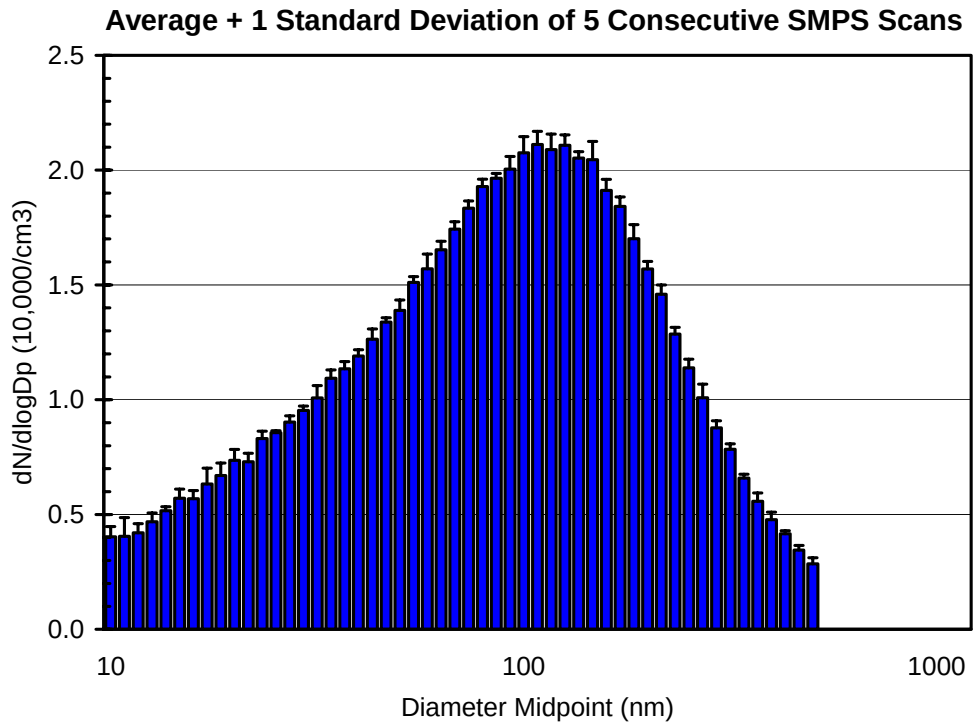

Figure 2. Consecutively measured particle size distributions. The standard deviation of the mean is very small, which illustrates that the size distribution was not changing significantly over time.

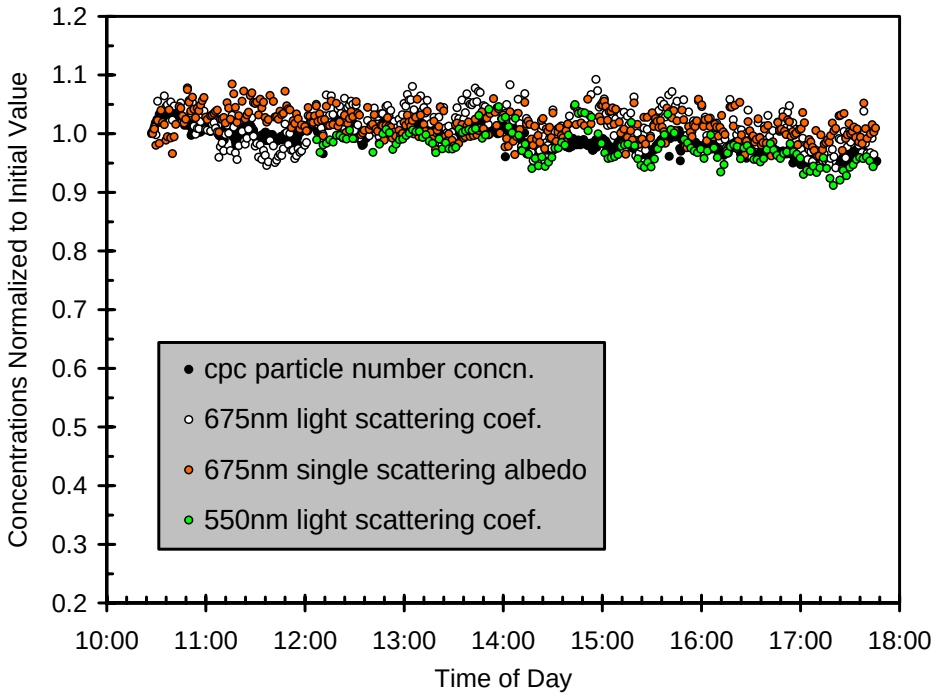

Figure 3. Particle number concentration, scattering coefficient (at 550 and 675 nm), and single scattering albedo (i.e., scattering/extinction ratio). The values of each parameter have been normalized to their values at the start of the experiment. A value of 1.0 during the seven hour experiment indicates that the measured parameter remained constant.

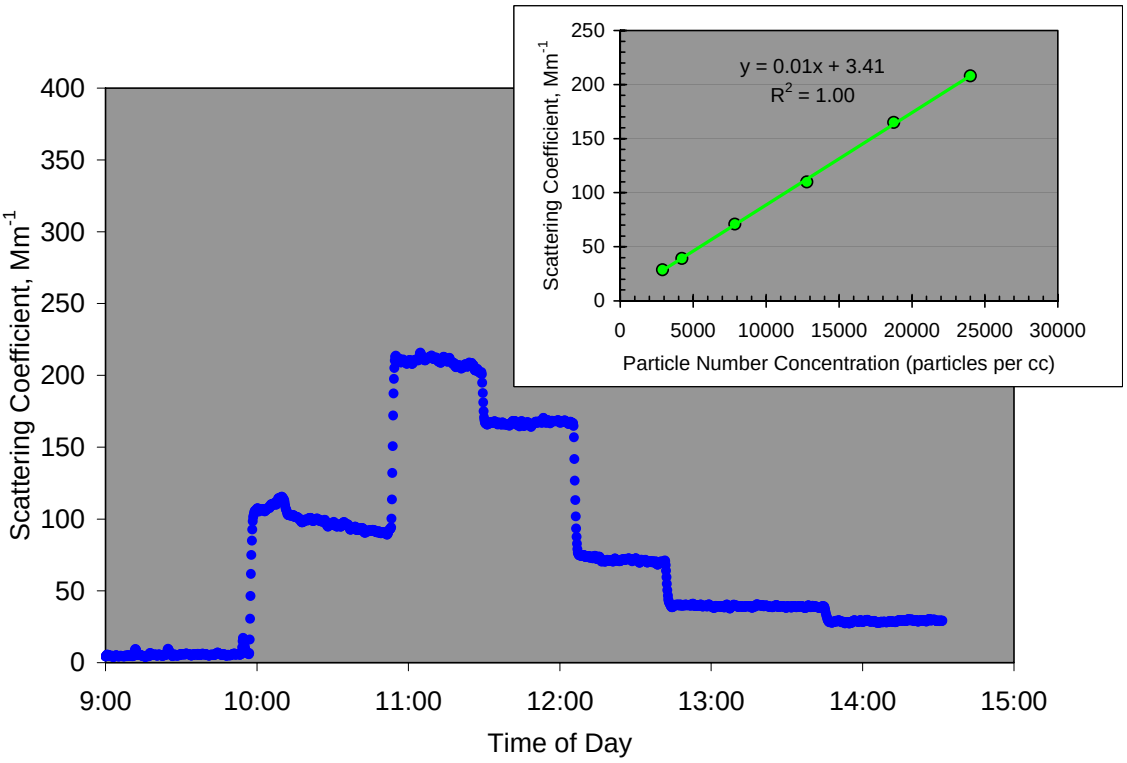

Figure 4. BC can be generated at various concentrations by changing air/fuel ratio. BC particle number concentration correlates well with light scattering coefficient, indicating that the scattering efficiency of BC remained constant.

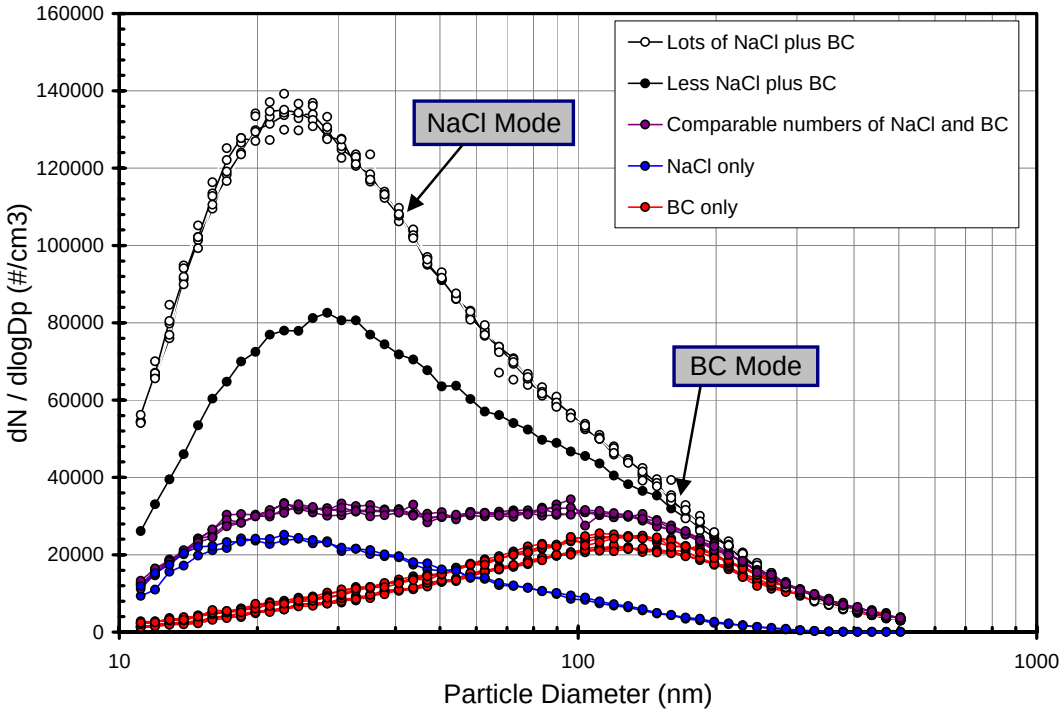

Figure 5. Size distributions of external mixtures of light absorbing (BC) and light scattering (NaCl) particles in varying proportions.

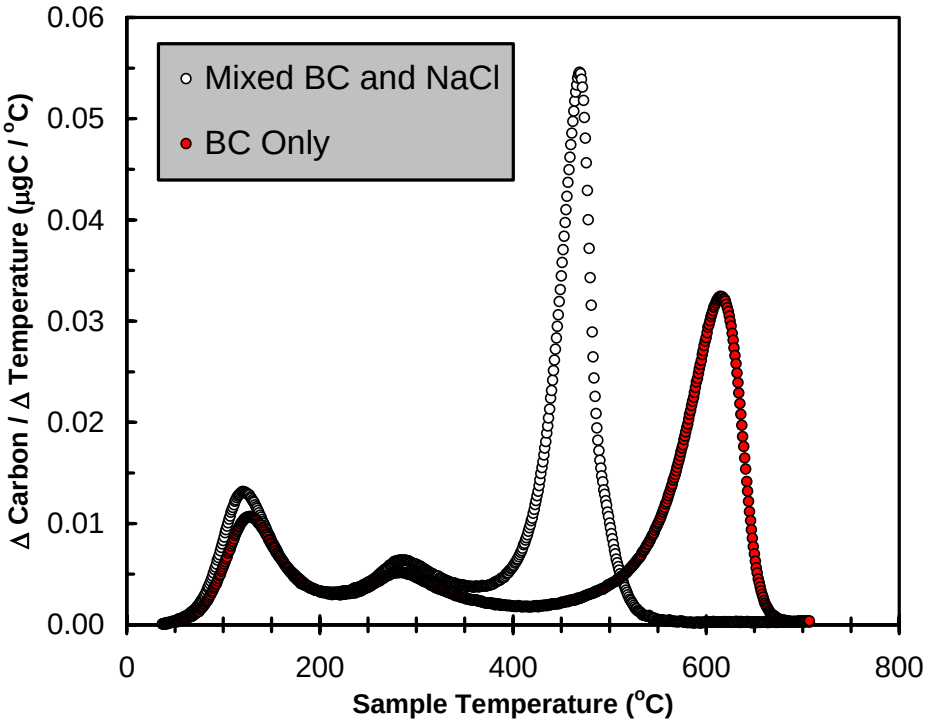

Figure 6. Carbon thermograms two quartz filter samples: BC alone and a mixture of BC and NaCl. The combustion temperature of BC is reduced by 150°C due to the presence of NaCl.

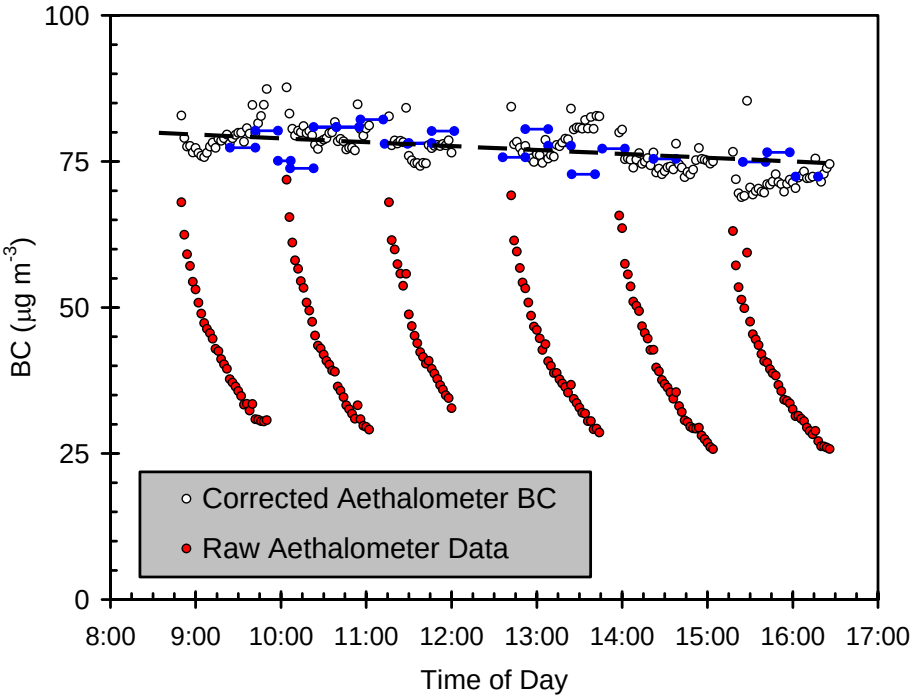

Figure 7. The aethalometer reports decreasing BC concentrations during each of its six measurement cycles over a seven hour experiment despite sampling a constant concentration of BC. Application of a modified calibration yields good agreement with BC concentrations derived from TOA of filter samples (shown in figure as solid blue horizontal bars, fit with a dashed black trend line).